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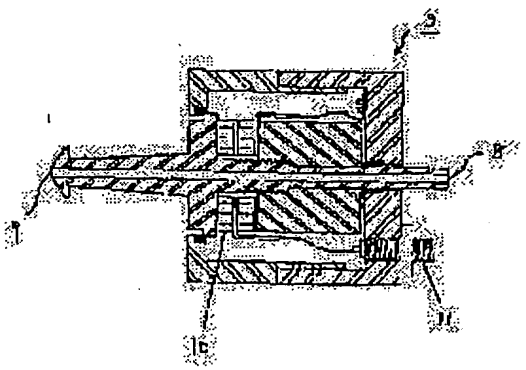
## (54) FORMATION OF TRANSPARENT CONDUCTIVE FILM

(57)Abstract:

PURPOSE: To avoid difference in thickness by applying ultrasonic vibration to a nozzle to spray and whereby reducing the diameter of an atomized metal compound and homogenizing it for effective adhesion to the surface of a substrate to be adhered.

CONSTITUTION: Ultrasonic energy is applied to a liquid metal compound 2 fed from an inlet port 8 to an atomized surface 9 by a piezoelectric device 10 to promote atomization. Effective atomization is achieved by designing the ultrasonic vibration so that the amplitude of the vibration reaches a maximum level at the atomized surface 9, and further grain refining and homogenization are achieved. A transparent conductive film in which difference in the thickness is drastically reduced, is thus formed. Since the grain refining with high atomization efficiency is achieved, the mass is reduced in relation to the momentum of the grain, and recoiling on the surface of a substrate to be adhered is small. Difference in the thickness is reduced thereby.



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## CLAIMS

[Claim(s)]
[Claim 1] The formation approach of the transparence electric-conduction film characterized by to make it blow off from the nozzle with which the liquefied metallic compounds for transparence electric conduction film were impressed to supersonic vibration using compressed gas in the shape of a fog, to spray the fog-like metallic compounds on the front face of the base for covering, to form the metallic-compounds film, and to form the transparence electric-conduction film by heating this metallic-compounds film and oxidizing it at 200-600 degrees C in the ambient atmosphere containing the inside of air, or oxygen after that.

[Translation done.]

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## DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the formation approach of the transparence electric conduction film without thickness nonuniformity with a spray method.
[0002]
[Description of the Prior Art] Recently, the transparence electric conduction film is briskly used for image sensors, the liquid crystal display, the touch panel, etc. the ingredient of this transparence electric conduction film -- In 2O3, SnO2, an In-Sn-O compound, TiO3, and Sb 2O3 etc. -- it is proposed and that part is already put in practical use. As the formation approach of this transparence electric conduction film, ** vacuum deposition, the ** sputtering method, ** reactive-sputtering method, ** spray method (evaporative decomposition), ** glow discharge oxidation style, ** CVD method, etc. are proposed.
[0003]
[Problem(s) to be Solved by the Invention] However, each of **, **, **s, **s, and **s needed vacuum devices, and the facility took great costs to them, and there were time amount and a trouble of **** for

cost also in the maintenance among the formation approaches of the transparence electric conduction film of these proposals. Furthermore, by these approaches, large-area-izing a membrane formation side also has the trouble of being difficult. And although target material is used in **, **, **, and **, it is not used for transparence electric conduction film, but all the prepared target material remains intact, and the trouble of raising the part and a manufacturing cost also usually has it 60 to 70%.

[0004] On the other hand, in the approach of **, the metaled organic substance and metaled complexes, such as In, Sn, and Sb, are applied by the spray. subsequently, the thing made to heat and oxidize at 200-600 degrees C in the ambient atmosphere containing the inside of air, or oxygen -- In 2O3 etc., if it is the approach of forming on a substrate and is this approach A pattern can be formed without FOTORISO by carrying out by using a metal mask etc. (or screen-stencil).

[0005] By the approach of this **, since vacuum devices were not needed, the above-mentioned trouble was cancelable, but on the other hand by using a spray, the nonuniformity of the thickness of the transparence electric conduction film arose, and there was a trouble that translucency and conductive variation were made between the transparence electric conduction film arranged by a large number by this.

[0006]

[Means for Solving the Problem] The formation approach of the transparence electric-conduction film of this invention is characterized by to make it blow off from the nozzle with which the liquefied metallic compounds for transparence electric conduction film were impressed to supersonic vibration using compressed gas in the shape of a fog, to spray the fog-like metallic compounds on the front face of the base for covering, to form the metallic-compounds film, and to form the transparence electric-conduction film by heating this metallic-compounds film and oxidizing it at 200-600 degrees C, in the ambient atmosphere containing the inside of air, or oxygen, after that.

[0007]

[Function] If it is the formation approach of this transparence electric conduction film, since supersonic vibration will be impressed to a nozzle, it equalizes, while the path of the generated fog-like metallic compounds becomes small, and such fog-like metallic compounds adhere to the front face of the base for covering efficiently, and can form the good transparence electric conduction film with which the nonuniformity of thickness became very small by this.

[0008]

[Example] Hereafter, the example of this invention is described.

[0009] Drawing 1 is the schematic diagram showing the formation approach of the transparence electric conduction film of this invention, and drawing 2 is a sectional view of a nozzle used for this formation approach.

[0010] In drawing 1 , 1 is a tank containing the liquefied metallic compounds 2 for transparence electric conduction film, and 3 is a spray. Moreover, 4 is a metal mask, 5 is a base for covering, and 6 shows the film for transparence electric conduction which is not heat-treated [ which was formed by the front face of the base 5 for covering ].

[0011] In such a configuration, it is moderately sent to a spray nozzle 3, these liquefied metallic compounds 2 serve as the shape of a fog 7 by this spray nozzle 3, and the liquefied metallic compounds 2 in a tank 1 face to the base 5 for covering. And membranes are formed by the predetermined configuration with the metal mask 4.

[0012] According to the nozzle 3 shown in drawing 2 , 8 is the inlet of the liquefied metallic compounds 2, 9 is a atomization side, and the liquefied metallic compounds 2 are conveyed toward the atomization side 9 from this inlet 8. Moreover, 10 is an input terminal for impressing a piezoelectric device and 11 to this piezoelectric device 10 electrically.

[0013] In the nozzle 3 of such a configuration, the ultrasonic vibrational energy generated by the piezoelectric device 10 joins the liquefied metallic compounds 2 conveyed toward the atomization side 9 from an inlet 8, and the atomization is promoted. It can be made to equalize, while being atomized

efficiently and carrying out grain refining more by this by designing so that the amplitude may become max to the supersonic vibration in respect of [ 9 ] atomization.

[0014] As a component of the above-mentioned liquefied metallic compounds 2, there is a metal organic substance metallurgy group complex etc., for example, there are the neo decanoic acid In, neo decanoic-acid Sn, octylic acid Sn, neo decanoic-acid Sb, octylic acid Sb, etc., it is independent, or these are combined and used. And this component is melted to solvents, such as a butanol, toluene, an acetylacetone, TORIKURORU trifluoro ethane, and Normal butyl acetate.

[0015] In this way, according to the formation approach of the transparence electric conduction film of the above-mentioned configuration, while carrying out grain refining more, the fog-like liquefied metal organic substance made to equalize can be applied to the front face of the base 5 for covering, and the film 6 for transparence electric conduction with which the nonuniformity of thickness became very small by this can be formed. Moreover, according to this formation approach, atomization effectiveness is high, since grain refining is carried out and mass becomes small by relation with the momentum of a particle, the recoil in the front face of the base 5 for covering becomes small, and the nonuniformity of thickness can form the film 6 for transparence electric conduction which became very small also by this.

[0016] Next, by heating this film 6 for transparence electric conduction, and oxidizing it at 200-600 degrees C, in the ambient atmosphere containing the inside of air, or oxygen, the transparence electric conduction film can be formed, neither translucency nor conductive variation is between the transparence electric conduction film arranged by a large number by this, and the uniform property was acquired.

[0017] this invention person etc. conducted the following experiment based on the above-mentioned technical thought.

[0018] (Example 1) first — the liquefied metallic compounds 2 — neo decanoic-acid indium In(C9 H19COO) 3 Neo decanoic-acid tin (C9 H19COO) Sn 4 mixture — using — the mixing ratio — the acetylacetone was used for the solvent of In/Sn=95/5, and the mixture of those as a rate is also at the atomic ratio of In and Sn. Moreover, the frequency of the supersonic vibration was set to the nozzle 3 at f= 120kHz, the middle particle diameter of 20 micrometers, and 50 micrometers of effective particle diameters using the SONOTEKKU system by Iwashita Engineering. the base 5 for covering — the Corning make — the glass substrate of **7059 was used.

[0019] According to the above-mentioned conditions, the thin film (film 6 for transparence electric conduction) of a sol-like organic metal compound was produced on the base 5 for covering by the formation approach of the transparence electric conduction film of drawing 1 .

[0020] Subsequently, the base 5 with which this film 6 for transparence electric conduction was formed was fed into the heater (not shown), it heated at 500 degrees C in air, heating oxidization of this film 6 for transparence electric conduction was carried out, and the chemical change was carried out to the transparence electric conduction film which consists of a multiple oxide of an indium and tin. This transparence electric conduction film is 10 micrometers or less in thickness, and resistivity became homogeneous membrane formation of 2 - 10 kilohm / ** within the limits. Moreover, the optical permeability in the light field of this transparence electric conduction film was as good as 90 - 100%, and uniform over the film surface moreover.

[0021] (Example 2) In the above-mentioned (example 2), when others formed the transparence electric conduction film which consists of a multiple oxide of an indium and tin by the same approach without impressing supersonic vibration to a nozzle, this resistivity was within the limits of 5 - 100 kilohm / **, and that value had large dispersion by the membranous part. And dispersion according [ the optical permeability in the light field of this transparence electric conduction film ] to 60 - 90% and a part was large, and became the film of inferior quality.

[0022] (Example 3) the above-mentioned (example 1) — setting — the liquefied metallic compounds 2 - - neo decanoic-acid antimony Sb(C9 H19COO) 4 Neo decanoic-acid tin (C9 H19COO) Sn 4 mixture — using — the mixing ratio — the acetylacetone was used for the solvent of Sn/Sb=92/8, and the mixture

of those as a rate is also at the atomic ratio of Sb and Sn. And when others formed the transparence electric conduction film which consists of a multiple oxide of antimony and tin by the same approach, it was two to 16 kilohm /**, and the optical permeability in the light field of this transparence electric conduction film was 93 - 100%, and the resistivity of each of this Rhine was homogeneous over this whole film.

[0023]

[Effect of the Invention] Since it is the spray method which impresses supersonic vibration to a nozzle according to the formation approach of the transparence electric conduction film of this invention the above passage It equalizes, while the path of the generated fog-like metallic compounds becomes small, and such fog-like metallic compounds adhere to the front face of the base for covering efficiently. By this Neither translucency nor conductive variation is between the transparence electric conduction film which could form the transparence electric conduction film with which the nonuniformity of thickness became very small, consequently was arranged by a large number, and the uniform property was acquired.

[0024] Moreover, when it was the formation approach of this transparence electric conduction film, vacuum devices were not needed, the needlessness of those facility costs was carried out, and the needlessness also of that maintenance was carried out, and it also became easy to large-area-ize a membrane formation side further.

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## DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] It is the explanatory view showing the formation approach of the transparence electric conduction film of this invention.

[Drawing 2] It is the sectional view of the nozzle shown in drawing 1 .

[Description of Notations]

2 .... Liquefied metallic compounds

3 .... Spray

5 .... Nozzle

6 .... Film for transparence electric conduction

9 .... Atomization side

10 ... Piezoelectric device

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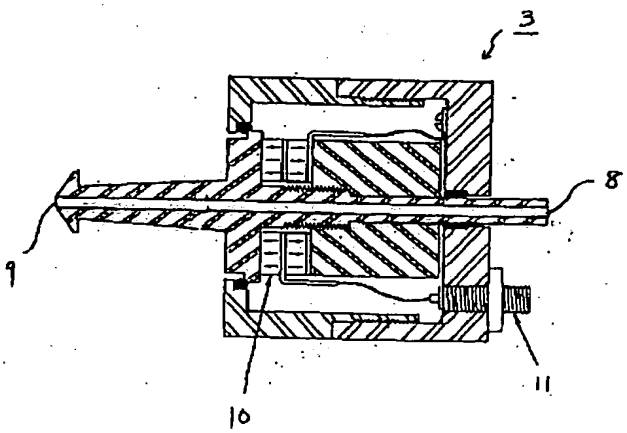
(54)【発明の名称】　透明導電膜の形成方法

(57)【要約】
【目的】複数の透明導電膜の間で透光性や導電性のバラツキがなく、均一な特性が得られた。
【構成】透明導電膜用の液状金属化合物を超音波振動が印加されたノズルを介して霧状にし、その霧状金属化合物を被着用基体の表面に吹き付けて金属化合物膜を形成し、その後、該金属化合物膜を空気中あるいは酸素を含む雰囲気中で２００～６００℃で加熱し酸化させることにより透明導電膜を形成することを特徴とする透明導電膜の形成方法。



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【特許請求の範囲】

【請求項１】透明導電膜用の液状金属化合物を圧縮ガスを用いて超音波振動が印加されたノズルより霧状に噴出させ、その霧状金属化合物を被着用基体の表面に吹き付けて金属化合物膜を形成し、その後、該金属化合物膜を空気中あるいは酸素を含む雰囲気中で２００～６００℃で加熱し酸化させることにより透明導電膜を形成することを特徴とする透明導電膜の形成方法。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明はスプレー法により膜厚ムラのない透明導電膜の形成方法に関するものである。

【０００２】

【従来の技術】近時、透明導電膜はイメージセンサー、液晶表示装置、タッチパネル等に盛んに用いられている。この透明導電膜の材料には$In_2O_3$、$SnO_2$、Ｉｎ－Ｓｎ－Ｏ化合物、$TiO_3$、$Sb_2O_3$等が提案され、その一部は既に実用化されている。この透明導電膜の形成方法として、①真空蒸着、②スパッタリング法、③反応性スパッタリング法、④スプレー法（噴霧熱分解法）、⑤グロー放電酸化法、⑥ＣＶＤ法等が提案されている。

【０００３】

【発明が解決しようとする問題点】しかしながら、これらの提案の透明導電膜の形成方法のうち、①、②、③、⑤、⑥はいずれも真空装置を必要として、その設備に多大な費用を要し、また、そのメンテナンスにも時間や経費を要すという問題点があった。更にこれらの方法では成膜面を大面積化することは困難であるという問題点もある。しかも、①、②、③、⑤ではターゲット材を用いるが、その用意したターゲット材のすべてが透明導電膜用に使われるのではなく、通常６０～７０％は未使用のままになり、その分、製造コストを高めるという問題点もある。

【０００４】これに対して④の方法では、Ｉｎ、Ｓｎ、Ｓｂ等の金属の有機物や錯体をスプレーで塗布し、次いで空気中あるいは酸素を含む雰囲気中で２００～６００℃で加熱して酸化させることにより$In_2O_3$等を基板上に形成するという方法であり、この方法であれば、メタルマスク等を使用することで（或いはスクリーン印刷）することによりフォトリソなしでパターンを形成することができる。

【０００５】この④の方法では、真空装置を必要としないので、上記の問題点が解消できるが、その反面、スプレーを使用することにより透明導電膜の厚みのムラが生じ、これにより、多数に配列された透明導電膜の間で透光性や導電性のバラツキができるという問題点があった。

【０００６】

【問題点を解決するための手段】本発明の透明導電膜の

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形成方法は、透明導電膜用の液状金属化合物を圧縮ガスを用いて超音波振動が印加されたノズルより霧状に噴出させ、その霧状金属化合物を被着用基体の表面に吹き付けて金属化合物膜を形成し、その後、該金属化合物膜を空気中あるいは酸素を含む雰囲気中で２００～６００℃で加熱し酸化させることにより透明導電膜を形成することを特徴とする。

【０００７】

【作用】この透明導電膜の形成方法であれば、超音波振動をノズルに印加しているので、発生した霧状金属化合物の径が小さくなるとともに均一化し、そのような霧状金属化合物が被着用基体の表面に効率的に付着し、これにより、厚みのムラがきわめて小さくなった良質の透明導電膜を形成することができる。

【０００８】

【実施例】以下、本発明の実施例を述べる。

【０００９】図１は本発明の透明導電膜の形成方法を示す概要図であり、図２はこの形成方法に用いられるノズルの断面図である。

【００１０】図１においては、１は透明導電膜用の液状金属化合物２が入ったタンクであり、３はスプレーである。また、４はメタルマスク、５は被着用基体であり、６は被着用基体５の表面に成膜された未加熱処理の透明導電用膜を示す。

【００１１】このような構成において、タンク１内の液状金属化合物２は適度にスプレーノズル３に送られ、このスプレーノズル３により該液状金属化合物２が霧状７となって被着用基体５に向かう。そして、メタルマスク４により所定の形状に成膜される。

【００１２】図２に示すノズル３によれば、８は液状金属化合物２の注入口、９は霧化面であり、この注入口８から霧化面９に向かって液状金属化合物２が輸送される。また、１０は圧電素子、１１はこの圧電素子１０に電気的に印加するための入力端子である。

【００１３】このような構成のノズル３において、注入口８から霧化面９に向かって輸送される液状金属化合物２に、圧電素子１０により発生した超音波振動エネルギーが加わり、その霧化が促進される。その超音波振動に振幅が霧化面９で最大になるように設計することにより効率的に霧化され、これにより、より細粒化するとともに均一化させることができる。

【００１４】上記液状金属化合物２の成分としては、金属有機物や金属錯体等があり、例えばネオデカン酸Ｉｎ、ネオデカン酸Ｓｎ、オクチル酸Ｓｎ、ネオデカン酸Ｓｂ、オクチル酸Ｓｂ等があり、これらを単独でもしくは組み合わせて用いる。そして、この成分をブタノール、トルエン、アセチルアセトン、トリクロルトリフルオロエタン、ノーマルブチルアセテート等の溶剤に溶かす。

【００１５】かくして上記構成の透明導電膜の形成方法

によれば、より細粒化するとともに均一化させた霧状液状金属有機物を被着用基体５の表面に塗布でき、これにより、厚みのムラがきわめて小さくなった透明導電用膜６を形成することができる。また、この形成方法によれば、霧化効率が高く、細粒化されるので、粒子の運動量との関係で質量が小さくなるので、被着用基体５の表面での反跳が小さくなり、これによっても厚みのムラがきわめて小さくなった透明導電用膜６を形成することができる。

【００１６】次にこの透明導電用膜６を空気中あるいは酸素を含む雰囲気中で２００～６００℃で加熱し酸化させることにより透明導電膜を形成することができ、これにより、多数に配列された透明導電膜の間で透光性や導電性のバラツキがなく、均一な特性が得られた。

【００１７】本発明者等は上記の技術的思想に基づき、下記の実験を行った。

【００１８】（例１）先ず液状金属化合物２には、ネオデカン酸インジウムＩｎ（$C_9H_{19}COO)_3$と、ネオデカン酸スズＳｎ（$C_9H_{19}COO)_4$との混合物を用いて、その混合比率はＩｎとＳｎの原子比率でもってＩｎ／Ｓｎ＝９５／５、その混合物の溶剤にはアセチルアセトンを用いた。また、ノズル３には岩下エンジニアリング株式会社製のソノテックシステムを用いて、その超音波振動の周波数は、ｆ＝１２０ＫＨｚ、中間粒子径２０μｍ、有効粒子径５０μｍに設定した。被着用基体５には、コーニング製＃７０５９のガラス基板を用いた。

【００１９】図１の透明導電膜の形成方法により上記条件に従って被着用基体５の上にゾル状の金属有機化合物の薄膜（透明導電用膜６）を作製した。

【００２０】次いで、この透明導電用膜６が形成された基体５を加熱器（図示せず）に投入し、空気中で５００℃に加熱し、この透明導電用膜６を加熱酸化し、インジウムとスズの複合酸化物からなる透明導電膜へ化学変化させた。この透明導電膜は厚み１０μｍ以下で、抵抗率が２～１０キロオーム／□の範囲内の均質な成膜になった。また、この透明導電膜の可視光領域での光学的透過率が９０～１００％と良好であり、しかも、膜面にわたって均一であった。

【００２１】（例２）上記の（例２）において、超音波振動をノズルに印加しないで、その他は同じ方法によりインジウムとスズの複合酸化物からなる透明導電膜を形



成したところ、この抵抗率は５～１００キロオーム／□の範囲内であり、その値は膜の部位によりばらつきが大きかった。しかも、この透明導電膜の可視光領域での光学的透過率が６０～９０％と部位によるばらつきが大きく、品質の悪い膜となった。

【００２２】（例３）上記の（例１）において、液状金属化合物２には、ネオデカン酸アンチモンＳｂ（$C_9H_{19}COO)_4$と、ネオデカン酸スズＳｎ（$C_9H_{19}COO)_4$との混合物を用いて、その混合比率はＳｂとＳｎの原子比率でもってＳｎ／Ｓｂ＝９２／８、その混合物の溶剤にはアセチルアセトンを用いた。そして、その他は同じ方法によりアンチモンとスズの複合酸化物からなる透明導電膜を形成したところ、この各ラインの抵抗率は２～１６キロオーム／□であり、また、この透明導電膜の可視光領域での光学的透過率が９３～１００％であり、この膜全体にわたって均質であった。

【００２３】

【発明の効果】以上の通り、本発明の透明導電膜の形成方法によれば、超音波振動をノズルに印加するスプレー法であるので、発生した霧状金属化合物の径が小さくなるとともに均一化し、そのような霧状金属化合物が被着用基体の表面に効率的に付着し、これにより、厚みのムラがきわめて小さくなった透明導電膜を形成することができ、その結果、多数に配列された透明導電膜の間で透光性や導電性のバラツキがなく、均一な特性が得られた。

【００２４】また、この透明導電膜の形成方法であれば、真空装置を必要とせず、その設備費用を不要し、また、そのメンテナンスも不要し、更に成膜面を大面積化することも容易になった。

【図面の簡単な説明】

【図１】本発明の透明導電膜の形成方法を示す説明図である。

【図２】図１に示すノズルの断面図である。

【符号の説明】

２・・・・液状金属化合物

３・・・・スプレー

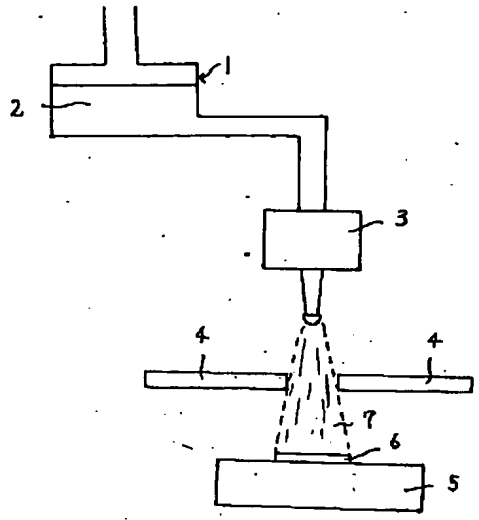
５・・・・ノズル

６・・・・透明導電用膜

９・・・・霧化面

１０・・・圧電素子

【図１】




【図２】